EFFECT OF VERY HIGH CENTRIFUGAL FIELDS ON THE RATE OF SELF-DIFFUSION OF POLYCRYSTALLINE SILVER

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ABSTRACT

This experiment outlines a technique for obtaining diffusion constants of metals at temperatures well below their melting points by the application of force fields of 160,000,000 times the acceleration of gravity with a magnetic-supported magnetic-driven ultracentrifuge. Three successive layers of silver were electro-deposited upon the cylinderical surface of a 0.05 cm diameter steel rotor. The inner layer (5.5×10^{-5} cm thick) and the outer layer (1.38×10^{-4} cm thick) consisted of ordinary silver, while the middle layer (5.5×10^{-5} cm thick) contained silver enriched with the radioisotope Ag^{110}. The rotor was suspended and spun in an evacuated chamber. The radial movement of the Ag^{110} was determined by counting the beta particles emerging through the periphery of the rotor by a scintillation crystal, photomultiplier, and pulse height analyzer circuit as a function of time. The results show that the self-diffusion constant for silver at seventy-two degrees centigrade is approximately 6 to 7×10^{-13} cm^2/sec. These techniques are also of value for the determination of the mechanism of diffusion. The results of this experiment indicate that the mechanism of self-diffusion in silver is the vacancy exchange mechanism.

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INTRODUCTION

The results of research in the field of diffusion of solid materials, besides giving a better insight to the behavior of solid materials, lend themselves to many applications in the field of metallurgy. Several metallurgical processes which involve diffusion are: carburizing, in which carbon diffuses into steel; nitriding; manufacturing of bimetallic strips which depend upon the adhesion resulting from the interdiffusion of the two metals and the rate of age hardening and transformation of metals. By relying more on purely scientific work, metallurgy is becoming less of an art and more of a science. It was therefore felt that some additional work toward the better understanding of the diffusion mechanism of metals could provide a worthwhile contribution to physics. The research results and diffusion theory based on them could also be applied to the field of metallurgy.

Because the time required for the diffusion of atoms through a certain distance increases as the temperature of the material is lowered from its melting point, the diffusion constants of metals at temperatures well below their melting points are very difficult to obtain. A method for increasing the rate of diffusion at these lower temperatures is by applying large directional forces. The ultracentrifuge techniques of applying extremely high directional forces to very thin films without the usual

attendant twisting moments and force concentrations, developed by Dr. J.W. Beams[1] makes possible the study of the diffusion properties of metals at temperatures far below their melting point.

The detection of diffusion is accomplished by either of two common procedures, the "direct" or the "indirect" method. The "direct" method consists of placing two substances in contact and maintaining them at an elevated temperature. This technique requires a long period of time at an elevated temperature to allow a measureable amount of diffusion to take place. The specimen is sectionalized, and the diffusion determined by chemical analysis of successive sections.

In the "indirect" method, a radioactive isotope is used for one of the specimens. Concentration of this material in the second specimen is determined by detection of the radioactivity. This method was first employed by von Hevesy, Seith, and Keil,[2] who used an alpha emitting lead isotope, Thorium B, to determine the self-diffusion of lead in a lead single crystal. As diffusion progressed the change in the rate of radioactive emission was used as an indication of the change in relative displacements of the atoms.

A combination of the application of centrifugal forces ranging to 700,000 times the acceleration of gravity

and the "indirect" diffusion detection method had previously been used in this laboratory for preliminary investigations of the self-diffusion rate of silver[3,4]. The results indicated that more enlightening information concerning the basic properties involved would be obtained if much greater forces were applied. Accordingly, this investigation was conducted by using the "indirect" detection method in conjunction with centrifugally applied force fields ranging to 160,000,000 times the acceleration of gravity.

CONSIDERATIONS OF DIFFUSION THEORY

Three possible simple mechanisms for the diffusion of the atoms of one metal, A, through a metallic solid, B, are:

1) The A atoms may individually diffuse through the interstices of the solid, B;

2) The A atoms may exchange position with the B atoms within the lattice; and

3) The A atoms may move into adjacent vacant positions in the lattice of the solid, B.

In the case of the first mechanism, the activation energy required to move an atom increases greatly as the size of the interstitial sites is diminished. These sites

are much smaller than the atomic size for metals forming substitutional alloys and therefore one would expect that only metals forming interstitial alloys would lend themselves to this type of mechanism.

The activation energy required for the second mechanism should be of the same order of magnitude as the cohesive energy because, during the exchange of positions, the two interchanging atoms would be forced closer together by the surrounding atoms of the lattice. The likelihood of this mechanism being responsible for diffusion is rather low considering the values of the activation energy obtained from numerous data. (This has been compiled by Seitz.[5])

The third mechanism for diffusion assumes that vacant sites, hereafter called vacancies, exist in the lattice of the material thereby creating a certain amount of disorder. Theoretical work in thermodynamics indicates that the disorder introduced by the vacancies in the lattice structure would result in an increase of entropy .

Although substitutional alloys are not expected to diffuse by the first mechanism, the problem of determining which of the other two mechanisms is responsible for their diffusion is still present. In fact, Zener[6] has proposed a combination of mechanisms, in which complex geometrical patterns of the motion of the atoms give rise to diffusion.

But regardless of the mechanism involved, the relative displacement of the atoms, A and B, must be known to determine the rate of diffusion. A classic example of determining the rate of diffusion by measuring the relative displacement was accomplished by Smigelskas and Kirkendall.[7] Molybdenum wires were embedded at the interface between copper and alpha brass. After maintaining the specimen at a high temperature for a long period of time, the molybdenum wires were found to have moved into the brass. Investigations of other face-centered cubic metal pairs revealed the same effect. This is considered an indication that neither the direct exchange mechanism nor the Zener theory are the chief processes of diffusion in these metals.

There is a strong relationship between temperature and the diffusion rate in both grain boundary and lattice diffusion. This dependency is expressed by a relation of the form, $D = \text{Const.}\ e^{-\frac{Q}{RT}}$ where R is the gas constant; T, the absolute temperature; and Q, the activation energy which must be supplied before an atom may move from one position to another. The quantity represented by D is called the diffusion constant.

It was shown by Johnson[8] that the self diffusion constant for silver differed for grain boundary and lattice

diffusion. This is in agreement with the theory of Chalmers[9] based upon the behavior of very pure tin in the vicinity of its melting point. His results indicated that the melting point of the material in the grain boundaries was slightly lower than that of the bulk material. From these results it was concluded that the transition layer of atoms in the grain boundaries was thermodynamically less stable than the interior atoms of the grains. This agreed with the previous remarks concerning increases of entropy with higher vacancy concentration.

The constant term in the expression previously given for the diffusion constant depends upon the metal and varies very slowly with temperature. The values for the activation energy as well as for this constant are found by fitting curves to experimental data.

Several investigations have been undertaken to determine the self-diffusion constants for silver by electrodepositing a radioactive silver layer on the surface of regular silver. Hoffman and Turnbull[10] found that the grain boundary diffusion constant for silver into high purity silver was independent of the grain size of the specimens. They found values of the constant and the activation energy of 0.03 cm^2/sec. and 20,200 calories per mole respectively, at temperatures around four hundred degrees Centigrade. Johnson[8] found values

of 0.895 and 45,950 in the case of lattice self-diffusion. In more recent work with silver, Turnbull and Hoffman[11] found new values for grain boundary self-diffusion of 0.14 and 19,700. They also determined that the diffusion rate along dislocation pipes produced by cold working the material may be identified with the low angle grain boundary diffusion constant, is independent of the angle of misorientation for angles less than thirty degrees, and is several orders of magnitude greater than the lattice self-diffusion rate.

In order to determine the diffusion constant from the observed change in the counting rate and the elapsed time, it was necessary to determine the concentration of the radioisotopic atoms as a function of time and position; introduce the absorption coefficient; and integrate this quantity over the entire thickness of the films.

The problem was attacked by assuming that the films consisted of a sea of grain boundaries and that the diffusion of the silver radioisotopic atoms took place by exchanging positions with the vacancies in the grain boundaries. This allowed the application of Fick's Laws for determining the concentration, C, of a solute in a solvent in terms of space-time coordinates. The situation was reduced to the one dimensional case by the use of a collimating slit which limited the area of the rotor

exposed to the crystal. Fick's Laws, reduced to the one dimensional form, become

$$J = -D\frac{dc}{dx}$$

$$\text{and } \frac{dc}{dt} = D\frac{d^2c}{dx^2}$$

where J is the diffusion current; D, the diffusion constant; and C, the concentration of the radioisotope.

The following assumptions were made to obtain a solution to the above equation that would most nearly depict the experimental conditions:

1) All diffusion took place through the grain boundaries as the lattice diffusion was negligibly small.

2) The grain boundaries acted as vacancy sources.

3) The radioisotope was evenly distributed at time zero between x equals 0.55 x 10^{-4} cm and x equals 1.10 x 10^{-4} cm.

4) All of the material that migrated to the free outer surface (x equals 2.48 x 10^{-4} cm.), passed through the surface and remained there under the influence of the centrifugal field.

5) All of the material that migrated to the inner silver surface in contact with the steel rotor, (x equals zero), would after a very long period of time migrate to the outer surface and remain there under the influence of the centrifugal field.

6) A uniform force field, F, acts in the positive x direction.

By applying the above assumptions to the Fick one-dimensional equations, the following equations and conditions were obtained:

$$C = 0 \qquad x = 2.48 \times 10^{-4}\,\text{cm} \quad \text{for all } t$$

$$J = -D\frac{dC}{dx} + \mu FC = 0 \qquad x = 0 \quad \text{for all } t$$

$$\text{and } \frac{dC}{dt} = D\frac{d^2C}{dx^2} - \mu F\frac{dC}{dx}$$

where μ is the transport function, D/RT; and F is the difference in the force applied to the two exchanging particles, $m(1-\rho V)\omega^2 r$. In the case of vacancy diffusion, ρ equals zero and F reduces to $m\omega^2 r$ where m is the mass of the silver radioisotope; ω the rotational velocity; and r, the radius of the rotor.

After solving these equations for the concentration; multiplying by the factor, $e^{\lambda x}$ and integrating over the entire thickness of the silver films; the following expression for the counting rate at any time, t, was obtained.

$$N(t) = e^{\mu}\Big[1 - \alpha\frac{e^{\frac{1}{2\alpha}}}{a_2 - a_1}\sum_{i=1}^{\infty} e^{-q_i t}\frac{8\alpha p_i}{1 + 2\alpha + 4\alpha^2 p_i^2}\, G\left(\tfrac{1}{2\alpha}, p_i, a_1, a_2\right)$$

$$+ \frac{1}{a_2 - a_1}\sum_{i=1}^{\infty} e^{-q_i t}\left(1 + \frac{1}{4\alpha^2 p_i^2}\right)\frac{8\alpha^2 p_i^2}{1 + 2\alpha + 4\alpha^2 p_i^2}\cdot\frac{1}{\left(\frac{1}{2\alpha} + \mu\right)^2 + p_i^2}$$

$$\Big[p_i e^{\frac{1}{2\alpha} + \mu} - \left(\tfrac{1}{2\alpha} + \mu\right)\sin p_i - p_i\cos p_i\Big]\, G\left(\tfrac{1}{2\alpha}, p_i, a_1, a_2\right)$$

This equation reduces to:

1) for t equals zero,

$$N_i = \frac{e^{-4a_2} - e^{-4a_1}}{4(a_2 - a_1)} = 1.035 ;$$

2) for a force field produced by a rotational velocity of 200,000 revolutions per second,

$$N_f = 1.1192 - 0.073 e^{-4.12 \times 10^7 DT} - 0.0002 e^{-3.63 \times 10^8 DT} ; \text{ and}$$

3) for a force field produced by a rotational velocity of 400,000 revolutions per second,

$$N_f = 1.1192 - 0.085 e^{-4.26 \times 10^7 DT} - 0.00016 e^{-4.03 \times 10^8 DT} + 0.0043 e^{-1.87 \times 10^9 DT} .$$

For comparison with the above effects, a calculation of the maximum change in the counting rate was made by considering only thermal diffusion. The calculations show that the maximum observable change in the counting rate would be only one half percent when complete equilibrium had been reached.

The mathematical details of this theory are given in Appendix II.

EXPERIMENTAL TECHNIQUE

The radioactive tracer technique for determining the positions of certain atoms within a solid material appeared to fulfill the requirements necessary for the determination of the effect of high centrifugal fields on the diffusion rate of silver. This tracer technique appeared more desirable than either the sectionalization or chemical analysis techniques in that it allowed successive data to be taken without damaging the films, during the period of time the forces were applied. The electrodeposition method for obtaining the desired films was selected in preference to the evaporation method as the films produced would have better adhesion properties and at the same time this method would present less of a radiation health hazard.

Since the investigation was to be carried out in very high centrifugal fields, of the order of 1.6×10^8 times the acceleration of gravity, the following preparation technique was developed to insure good adhesion of the films to the steel rotor. The rotor was:

1) immersed in an acid cleaning and etching solution for five minutes to thoroughly cleanse and lightly etch the surface of the rotor. (this solution was prepared by mixing 28 ml. of sulphuric

acid with 8 ml. of water to which was added 1.6 ml. of hydrochloric acid and 33 ml. of glycerine);

2) immersed in a saturated aqueous sodium carbonate solution to neutralize the acid;

3) rinsed with distilled water and allowed to air dry;

4) electroplated for thirty seconds at 0.75 ma. in a silver strike solution[12] to give a very fine layer of silver with excellent adhesion properties (this solution was prepared by dissolving 432.5 mg. of silver cyanide and 22.0 grams of sodium cyanide in 500 ml. of distilled water);

5) electroplated for thirty seconds at 0.15 ma. in a silver cyanide solution[13] (this solution was prepared by dissolving 15.0 grams of silver cyanide, 20.5 grams of potassium cyanide, and 22.5 grams of potassium carbonate in 500 ml. of water);

6) electroplated for thirty seconds at 0.15 ma. in a silver cyanide solution enriched with the silver radioisotope 110 (this solution was prepared by dissolving 155 mg. of silver cyanide which contained 86 mg. of the radioisotopic silver, 170 mg. of potassium cyanide, and 186 mg. of potassium carbonate in 4.2 ml. of water); and

7) electroplated for seventy-five seconds at 0.15 ma. in the silver cyanide solution described in 5) above.

The thickness of the films was determined from the following equation derived from Faraday's Laws

$$T = \frac{Mat}{1000 F \rho A}$$

where T is the thickness of the film in centimeters; M, the molecular weight of silver; a, the current in milliamperes; F, the Faraday constant; ρ the density of silver; A, the area to be plated; and t, the plating time in seconds. The current density was maintained constant at 17.2 ma./cm^2 for all quantitative plating. The various layer thicknesses were obtained by varying the plating time. The thickness of the layer obtained from the strike solution could not be calculated from the above formula as a result of the extremely high cyanide concentration, but was determined gravimetrically to be of the order of 10^{-6} cm. This provided an extremely thin, highly adhesive bond for the subsequently applied thicker films. The thickness of the first film of ordinary silver and the film enriched with the silver radioisotope was 5.5×10^{-5} cm. and the thickness of the outer film, or overlay, was 1.38×10^{-4} cm. Microscopic examination revealed that the films prepared in the above manner were polycrystalline with a grain size considerably less than one micron.

The energy spectra of the beta ray emmission from the plated rotors were obtained by means of a scintillation crystal, energy discriminator and counting device, described under "Description of Apparatus." A typical energy spectrum is shown in Figure 1. Since silver 110 emits beta rays of both 0.53 and 0.087 Mev., it was necessary to establish which energy beta rays were being observed. An energy spectrum of Cesium 137 which emits a single beta ray of 0.51 Mev. was taken. The hump of the Cesium spectrum was found to lie at about the same energy range as that of the silver spectra, establishing that the observed beta rays from the silver emmissions were the 0.53 Mev beta rays.

It was noted that by varying the thickness of the overlay the counting rate at each energy level was altered in such a manner as to result in a vertical displacement of the curve. No shift of the energy range of the hump in the curve was detected. Therefore, the change in the counting rate in an energy band which included this hump was selected as the parameter for determining the movement of the radioactive atoms. This band ranged between two energy levels at which the counting rates were approximately equal and the slopes of the curves were approximately equal and of opposite sign. Referring to Figure 1, this band

ranged from 10.0 to 17.0 volts (pulse height analyzer settings).

To obtain an absorption coefficient which would account for experimental conditions such as scintillation crystal geometry, surfaces obtained by the plating techniques, and others, eight rotors were plated with the radioisotope. The number of counts in the energy band described above was totaled during a six minute period for each rotor. The rotors were then plated with various thicknesses of overlay and the number of counts in the band of each rotor were again totalled during a six minute period. A control rotor, consisting of a rotor plated with a thick layer of the radioisotope and covered with a very thin coating of polystyrene, was counted each time a test rotor was counted. The decay of the silver radioisotope and the drift in the counting equipment were compensated for by adjusting the number of counts of the test rotor at any time by the ratio of the actual number of counts of the control rotor at that time to its value at the time of the initial counting of the test rotor. The data is tabulated in Table I. The spectrum of each rotor was checked again and no lateral shift of the energy hump was ascertainable. An average absorption coefficient of 4.57×10^2 reciprocal centimeters was obtained

from this investigation as illustrated in Appendix II.

The temperature of the rotors under various conditions was determined by means of Tempil sticks. The material, which is of a powdery polycrystalline form when applied to the rotor, melts at a particular temperature and becomes a deep-colored amorphous mass. The sticks were calibrated in the vacuum system by comparison with a temperature indication obtained from an iron-constantan thermocouple and Rubicon potentiometer. The rotor was heated by radiation from a tungsten coil located in the vacuum system. The melting point of the sticks in the vacuum was found to agree very closely with their rated melting point in air. The rotors were then marked with the sticks, supported by a small fiber in the test chamber, and subjected to various fields and conditions. The data is tabulated in Table II. It was found that the maximum temperature attained by the rotor was about 72 degrees centigrade. Approximately ten degrees of this temperature rise resulted from the radiation of the speed detection light source.

Several tests were made with rotors, plated as outlined in the preparation paragraph above, held at a constant temperature of seventy-two degrees centigrade in an oven. The rotors were counted at various intervals during the seventy two hour period of the runs.

Tests using the centrifuge were conducted in the following manner. The test rotor was plated with the various films, the number of counts in the selected energy band was totaled for a period of time, and the rotor was then placed in the centrifuge. The control rotor was then counted. The test rotor was accelerated to the desired speed. At appropriate time intervals the rotor was decelerated, removed from the centrifuge, and its energy band count totalled. The energy band count of the control rotor was also totalled at this time. The test rotor was placed in the centrifuge again and accelerated to the desired speed. After adjusting the number of counts of the test rotor, as discussed above, the ratio of its adjusted number of counts to its initial number of counts was computed.

Tests were conducted using rotational velocities of two hundred thousand and four hundred thousand revolutions per second. The data are tabulated in Tables III and IV, and shown in Figures 2 and 3. The effects of the varying force fields applied during the acceleration and deceleration periods were compensated for by computing an effective time that the rotor was at the desired speed. This is illustrated in Appendix II.

APPARATUS

The apparatus used in this investigation can be subdivided into three parts:

1. The plating apparatus for electrodepositing the silver films on the rotors.
2. The ultracentrifuge and related equipment used to apply large centrifugal forces on the test rotors, and
3. The apparatus used to detect and count the radioactive emmissions from the test rotors.

Plating Apparatus

A water bath kept at constant temperature by a mercury thermoswitch controlled nichrome heating element maintained the plating solution at the proper plating temperature. The framework holding the plating solution beaker in the temperature bath was designed to allow rapid removal of the beaker and insertion of the radioactive plating solution container.

The radioactive plating solution was enclosed in a thick brass container to lessen the amount of radiation exposure to the experimenter. A platinum anode was employed to reduce to a minimum any variations in the ratio

of radioactive silver to nonradioactive silver concentrations in the solution. A tight fitting brass cap on the solution container kept evaporation of the solution to a minimum during storage.

The Centrifuge

A magnetic suspension, magnetic driven ultracentrifuge was designed and constructed to support and spin very small rotors with rotational velocities in excess of one million revolutions per second. Figure 4 shows an overall view of the centrifuge and related equipment. Figures 5 and 6 show schematic cross-sections of the centrifuge proper.

The support system consisted of a large iron core solenoid mounted above the rotor to supply the support field, and a very small sensing coil also mounted above, but very close to, the rotor to detect changes in the vertical position of the rotor. This sensing coil was a component of the grid tank circuit of a tuned-grid-tuned-plate oscillator, the output of which controlled the current flowing through the support solenoid. The sensing coil consisted of one hundred thirty turns of fifteen ten thousandths inch enameled copper wire with an inside diameter of one thirty-second inch and an outside diameter

of three-sixteenths inch. As the rotor changed its vertical position, the inductance of the grid tank coil was changed, detuning the oscillator. This resulted in an oscillator output signal which was a function of the rotor's vertical position. The amplified signal was fed through a phase shift network to minimize overshoot and to increase vertical stability. The support circuit is shown in Figure 7. Figures 8 and 9 show the power supplies used with the support circuit.

Horizontal oscillations were suppressed by a combination of two procedures. The first procedure was to position the rotor concentrically with the sensing coil and the magnetic support field. This was accomplished by changing the position of the movable iron core in the support solenoid. This adjustment was very critical. The second procedure was to place a very fine wire damping needle immersed in light oil under the rotor chamber as shown in Figure 5. It was later discovered that a long thin rod of soft iron, substituted under the chamber for the wire damper, shaped the magnetic support field sufficiently to provide excellent damping properties.

The drive circuit consisted of a Hartley oscillator operating at a fixed frequency of 1.3 megacycles which fed a signal into a phase splitting network. The two signals, ninety degrees out of phase, were amplified and

applied to two sets of drive coils. The four coils were positioned symmetrically around the chamber. The coils were wound in conical shape to provide the maximum number of ampere-turns at a minimum distance from the rotor and each set was tuned to maximum resonance by adjusting parallel connected trimmer capacitors. The amount of acceleration was controlled by varying the cathode level of the power amplifiers. The induced eddy currents in the rotor from the rotating magnetic field caused the rotor to accelerate. Accelerations of thirty thousand revolutions per second per minute were not uncommon and a velocity of one million forty-five thousand revolutions per second was attained before the rotor exploded. The circuit diagram for the drive circuit is shown in Figure 10. A conventional 300 volt D.C. regulated power supply with an output of 400 milliamperes at one percent regulation was used for the drive circuit. Its circuit is shown in Figure 11.

The speed determination of these small rotors rotating at very high velocities presented a challenging problem. This was overcome by focusing light from a D.C. source on the surface of the rotor through the open core of one of the drive coils. The reflected light was gathered and transferred to a photomultiplier tube by a

Lucite light pipe. This also cut down the background level of the photomultiplier due to stray light. One half of the rotor surface was then darkened with India Ink to provide a greater change in intensity of light reflected to the photomultiplier as the rotor revolved. The output of the tube was then beat against a sine wave output from a Hewllet-Packard 650A Test Oscillator on an oscilloscope. By noting the resulting Lissajous pattern, the speed was determined. The test oscillator was calibrated against the standard frequencies of WWV.

A conventional vacuum system consisting of a mechanical fore pump, a dryer containing phosphorous pentoxide crystals, an oil diffusion pump and a fore pressure thermocouple gauge was used to attain vacuums of the order of 10^{-6} mm. of mercury. The system incorporated a high vacuum stop cock, ground glass joint, and an air-predrying inlet system which allowed removal and replacement of the rotor with minimum loss of time for the pumps to reestablish the operating vacuum level.

The one half millimeter diameter rotors used in this experiment were made by polishing 0.020 inch piano wire to a diameter of 0.0197 inch or 0.5 mm., then cutting off lengths approximately one millimeter long, inserting them in a predrilled thin steel plate and grinding both

surfaces of the rotors and plate to a thickness of 0.0168 inch. These dimensions provided a configuration of the rotor that was very stable while spinning. The rotors were then punched from the plate when desired for use.

Beta Ray Counting Equipment

The beta ray counting apparatus, shown in Figure 12 and schematically in Figure 13, consisted of the following:

1. a pedestal for positioning the rotor, a stilbene scintillation crystal and a photomultiplier tube;
2. a linear amplifier;
3. a pulse height analyzer;
4. a scaler; and
5. a timer.

The rotor was positioned at the same place in front of the stilbene crystal each time it was counted by placing it on a very small diameter pedestal. It was found to be almost impossible to position the rotor so that the identical surface area of the rotor was presented at the same angle to the crystal surface. Therefore, the pedestal was rotated by a one RPM motor which operated automatically when the "count" switch on the

scaler was engaged. This necessitated the use of integral numbers of minutes in the counting periods to insure that the rotor was turned through complete revolutions. A seven thirty-seconds inch lead shield was mounted between the rotor and the stilbene crystal. A collimating slit consisting of a size eighty drill hole in the lead shield limited the area of the cylinder seen by the scintillation crystal.

A thin stilbene crystal was selected for the scintillation crystal because of its relative insensitiveness to gamma radiation and its linear response characteristics for electrons with energies above 100 kilovolts.[14] A thickness of one half millimeter was selected to provide an escape peak for the 0.53 Mev. electrons which have a range of 0.86 mm. in stilbene. A thirty-five hundred thousandth of an inch aluminum foil mounted between the lead shield and the crystal served both to absorb 0.033 Mev. of the energy of the beta rays striking the crystal,[15] and to reflect the photons emitted in the crystal back to the photomultiplier tube. A potential of 1500 V.D.C. was supplied to a DuMont 6291 photomultiplier tube by a neon glow tube regulated power supply. This produced less noise and better stability of the dynodes than could be obtained by operating the tube from a battery pack. A

cathode follower was used to match the impedance of the photomultiplier tube to the coaxial cable carrying the signals to the linear amplifier.

The linear amplifier consisted of an amplifier section similar to the Model 204 C Linear Amplifier, Atomic Instrument Company, and a 300 volt stabilized power supply[16] capable of delivering 150 ma. A 50 cubic foot per minute centrifugal blower provided air circulation through the chassis. A thermostatically controlled heating element mounted in the airstream under the amplifier section provided a constant temperature of the amplifier components, thereby stabilizing the amplifier gain.

An Atomic Instrument Company Model 510 pulse height analyzer was used to select the energy range desired. The number of pulses received from the analyzer was registered on an Atomic Instrument Company Model 1030A binary scaler.

The time interval for the counting period was determined by noting the number and tenths of seconds registered on a Precision Scientific Company "Time It" timer. The timer operated whenever the "count" switch on the scaler was engaged.

A more detailed description of the above equipment and a discussion of the development and adjustment of the components has been given by Kinsel.[17]

RESULTS AND DISCUSSION

The results of this investigation are twofold: first, they give an indication as to the mechanism involved in silver self-diffusion; and second, they point out a method for obtaining the self-diffusion constants of metals at temperatures well below their melting points.

The theoretical calculations indicated that the maximum change in the counting rate for rotors with no applied centrifugal fields should be about one half percent. This trend toward higher counting rates was masked by the statistical error of 1.4 percent and consequently was not detected.

On the other hand, the observed counting rate fpr those rotors which were subjected to high centrifugal fields increased from three to five percent. It is conceivable that such an increase could be attributed to partial losses of the ordinary silver overlay, but microscopic examination of the films both before and after centrifugation appeared to rule out this possibility. This change apparently must be due to the effect of the centrifugal field on diffusion.

Of the three types of diffusion mechanisms considered, it should be noted that diffusion by the third mechanism would be the foremost factor in producing any noticeable effect of the centrifugal field. For the first mechanism (interstitial diffusion) the perturbation applied to the activation energy would be negligibly small because the centrifugal force, large as it is, is still small in comparison with the interatomic forces. For the second mechanism (the exchange of position by two atoms) the difference in the mass between the radioisotopic silver and the ordinary silver is approximately two percent. Thus, essentially the same perturbation would be applied to both types of atoms. However, for the third mechanism (the exchange of an atom with a vacancy) the difference between the masses of the two exchanging particles, the atoms and vacancies, is at its maximum; and if the centrifugal field is to have any effect upon the rate of diffusion, it should be most apparent with this mechanism. Considering the relatively short time in which the counting rate became evident, it would appear that the self-diffusion of silver is accomplished by the exchange of position of an atom and a vacancy.

The possibility of ordinary sedimentation in the latter two cases, each of which have a mass difference,

should be considered. The difference of the masses of the particles exchanging positions is two atomic mass units for the second mechanism and one hundred ten for the third mechanism. Therefore, the sedimentation rate of the third mechanism would be expected to be 55 times that of the second. Thus, at any time, t, one would expect that 55/56 of the total effect of any sedimentation would have resulted from the third mechanism.

Figures 2 and 3 represent a plot of the equations developed in the Theory Section for the change in counting rate versus time for several arbitrarily chosen diffusion constants. The experimental data points are superimposed. It can be seen in Figure 2 that the curves plotted for $D = 6 \times 10^{-13}$ and $D = 7 \times 10^{-13}$ fit the points the best. In Figure 3 it can be seen that the curves corresponding to D equals 6 or 7×10^{-13} fit the experimental points best. From these two separate conditions, rotor speeds of 200,000 and 400,000 revolutions per second, the diffusion constant is found to be in the neighborhood of 6 to 7×10^{-13} centimeters squared per second. Upon inserting the value of the temperature maintained during this investigation, seventy-two degrees Centigrade, in the expression obtained by Turnbull and Hoffman[11] for the grain boundary self-diffusion constant of silver at temperatures

around four hundred degrees Centigrade, a value of 7×10^{-13} centimeters squared per second is obtained.

However, examination of the curves of Figures 3 and 4 show that there is a definite difference in rate of change of slope between the curves and the obtained data. There is need for a more comprehensive theory, which includes additional conditions such as the difference in the vacancy migration rate toward the center of the rotor and the vacancy formation rate in the grain boundaries, to fully explain the data.

ACKNOWLEDGEMENTS

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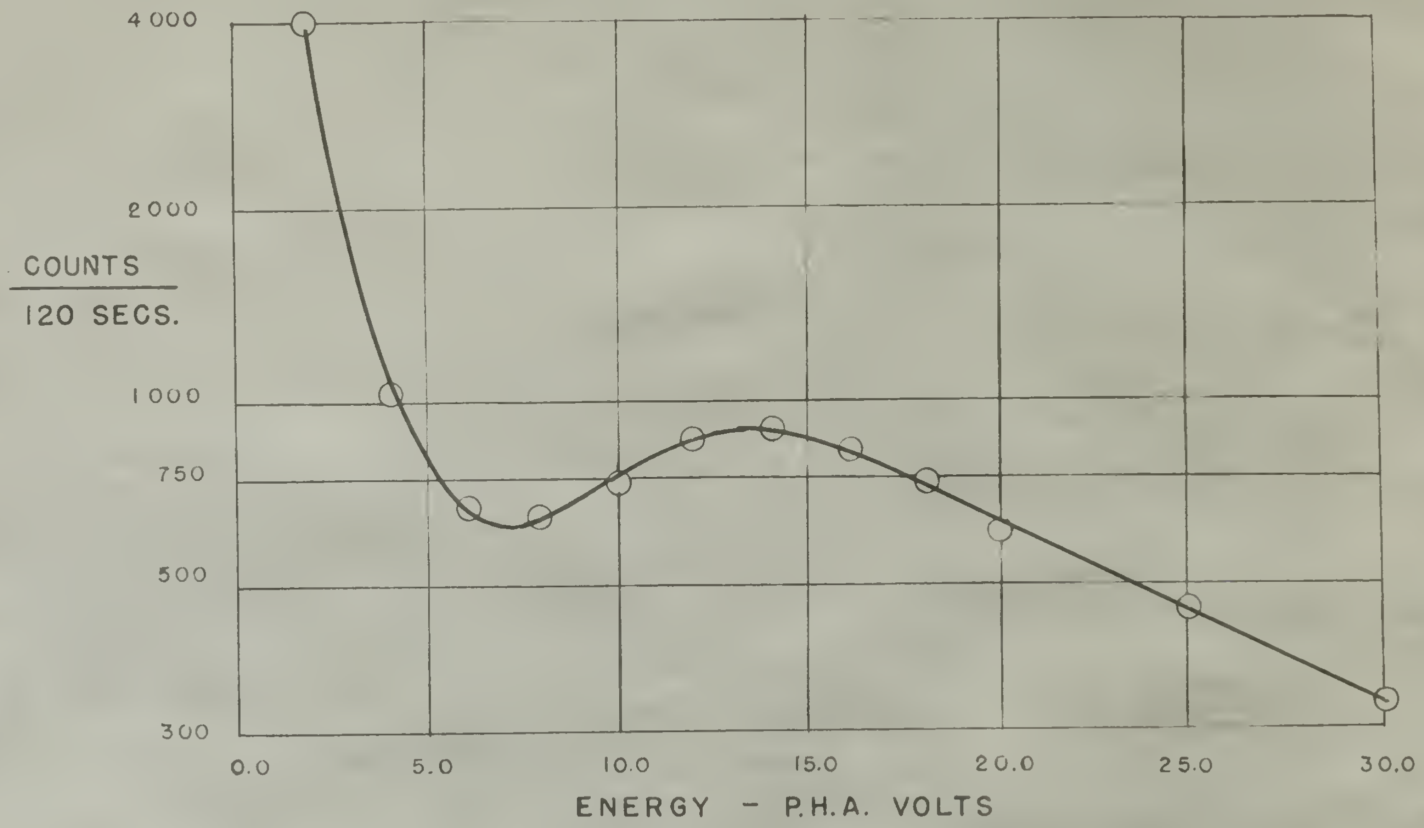
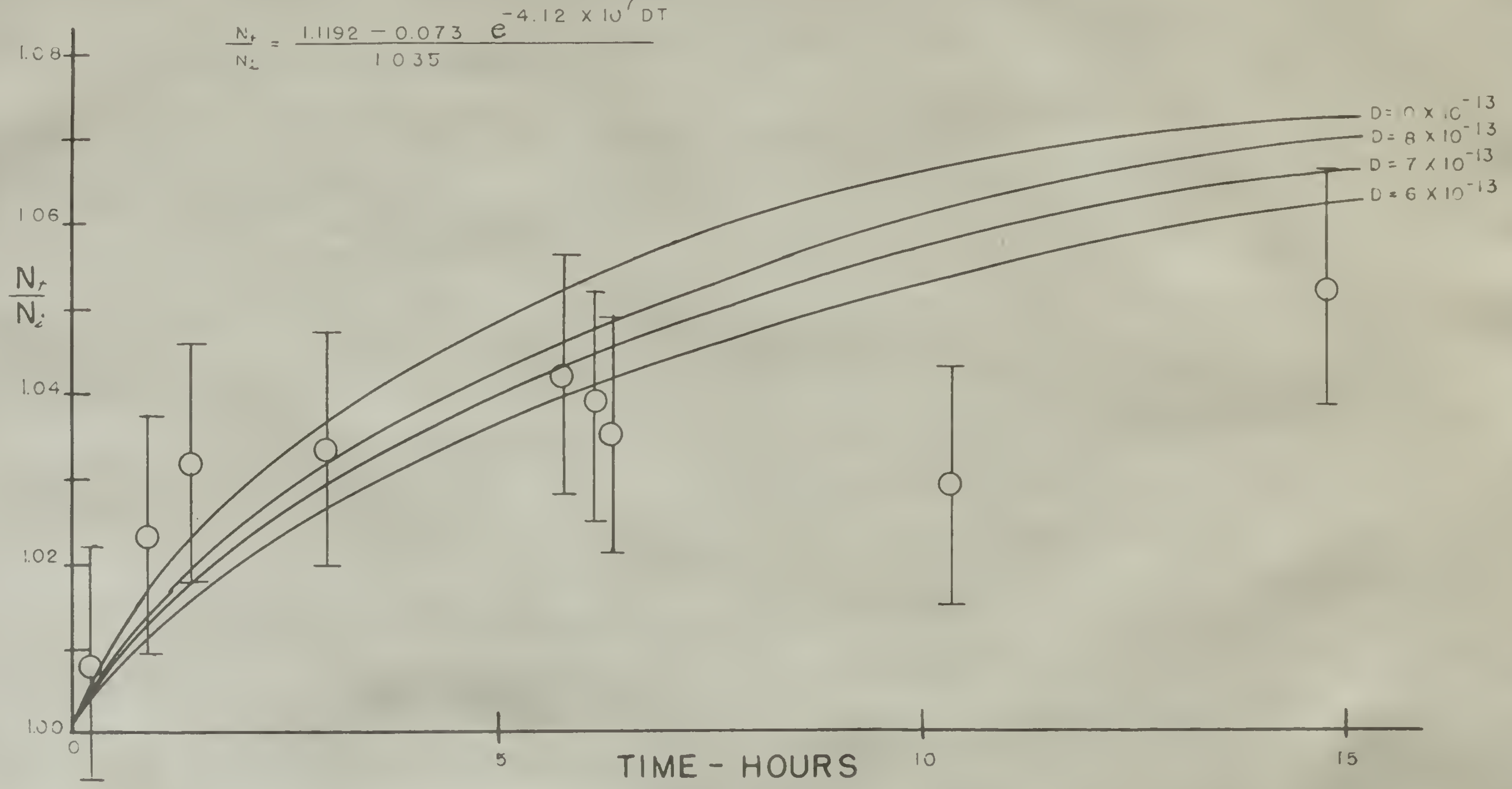


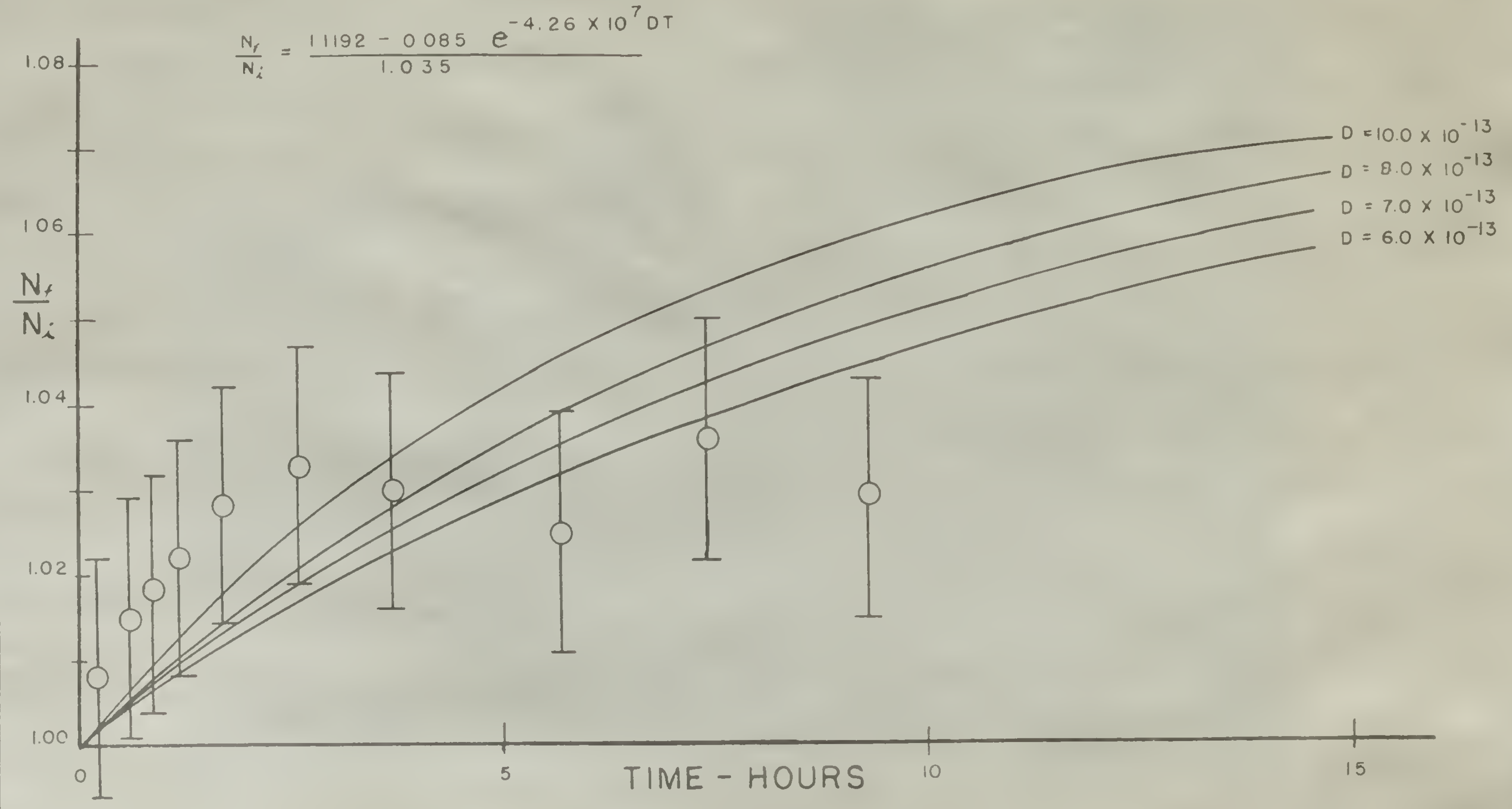
TYPICAL ENERGY SPECTRUM OF A PLATED ROTOR

FIGURE 1



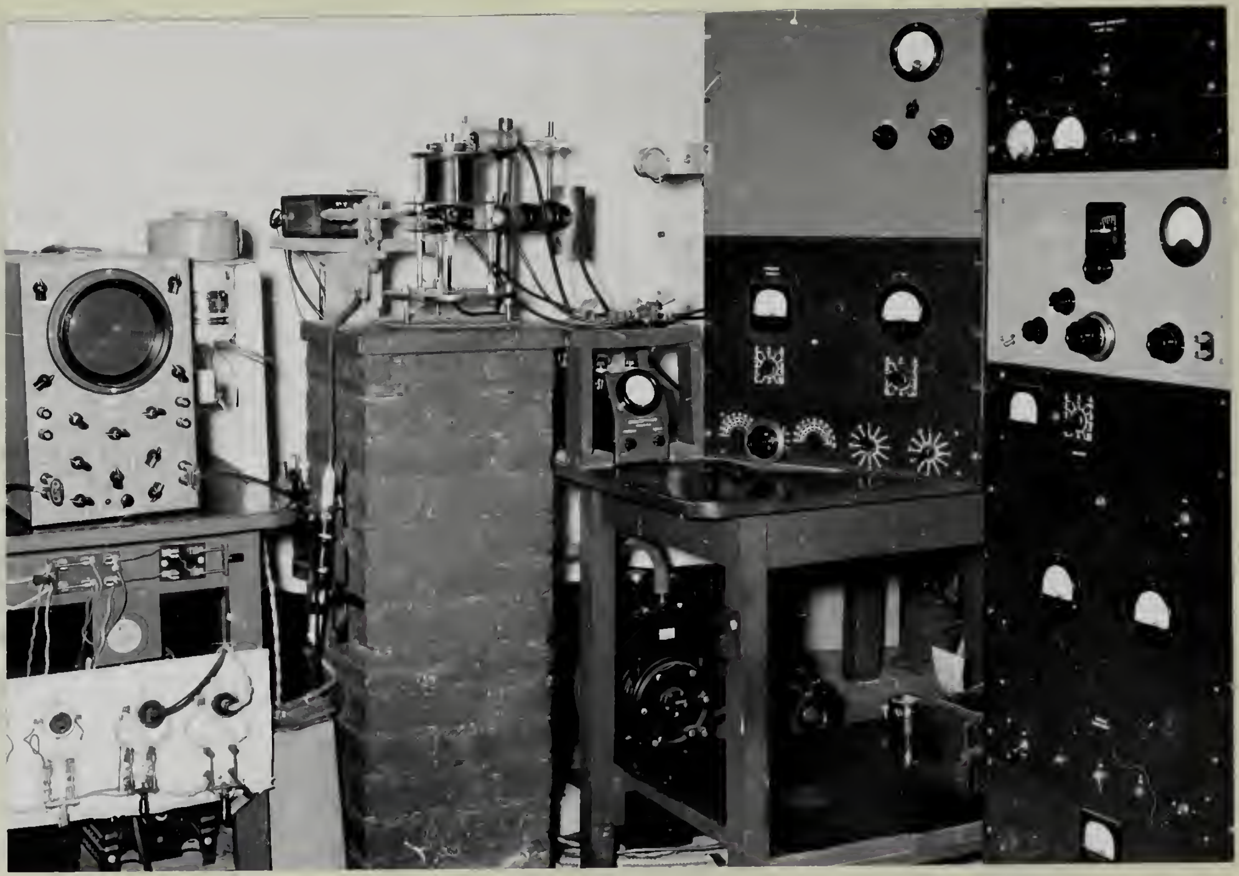
CHANGE IN COUNTING RATE VS. TIME
(200,000 RPS, 72°C)

FIGURE 2



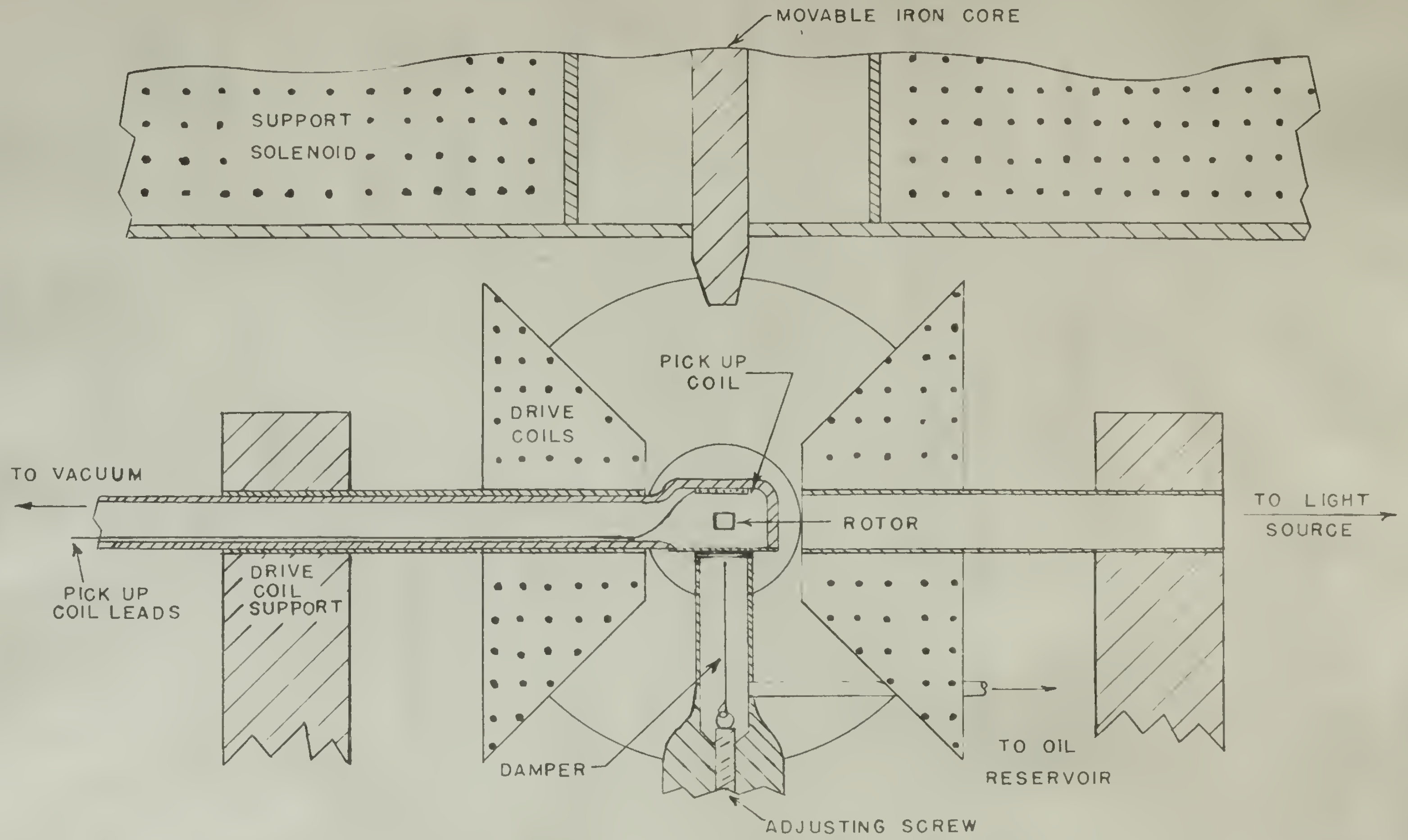
CHANGE IN COUNTING RATE VS. TIME
(400,000 RPS, 72°C)

FIGURE 3



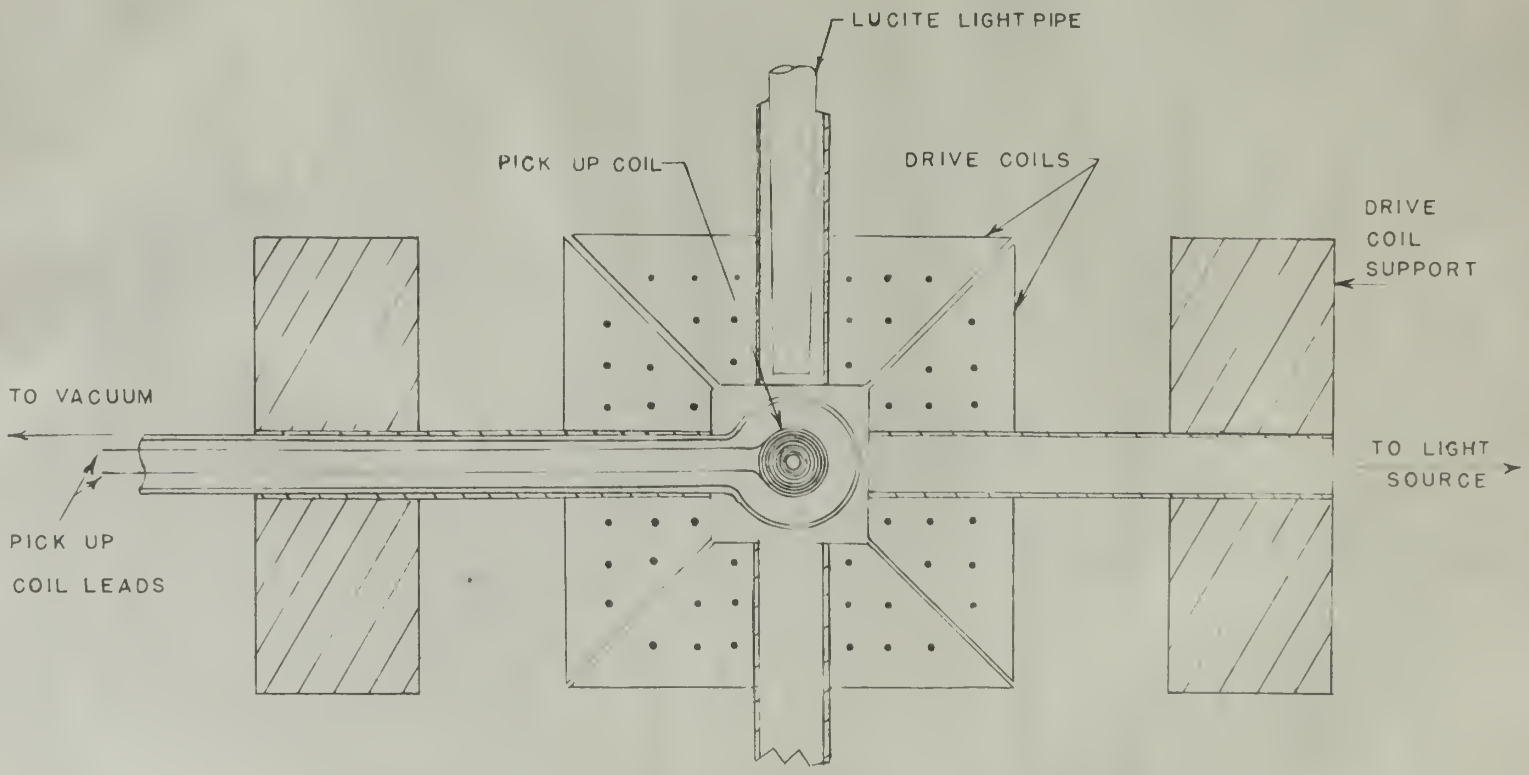
THE ULTRACENTRIFUGE

[illegible]



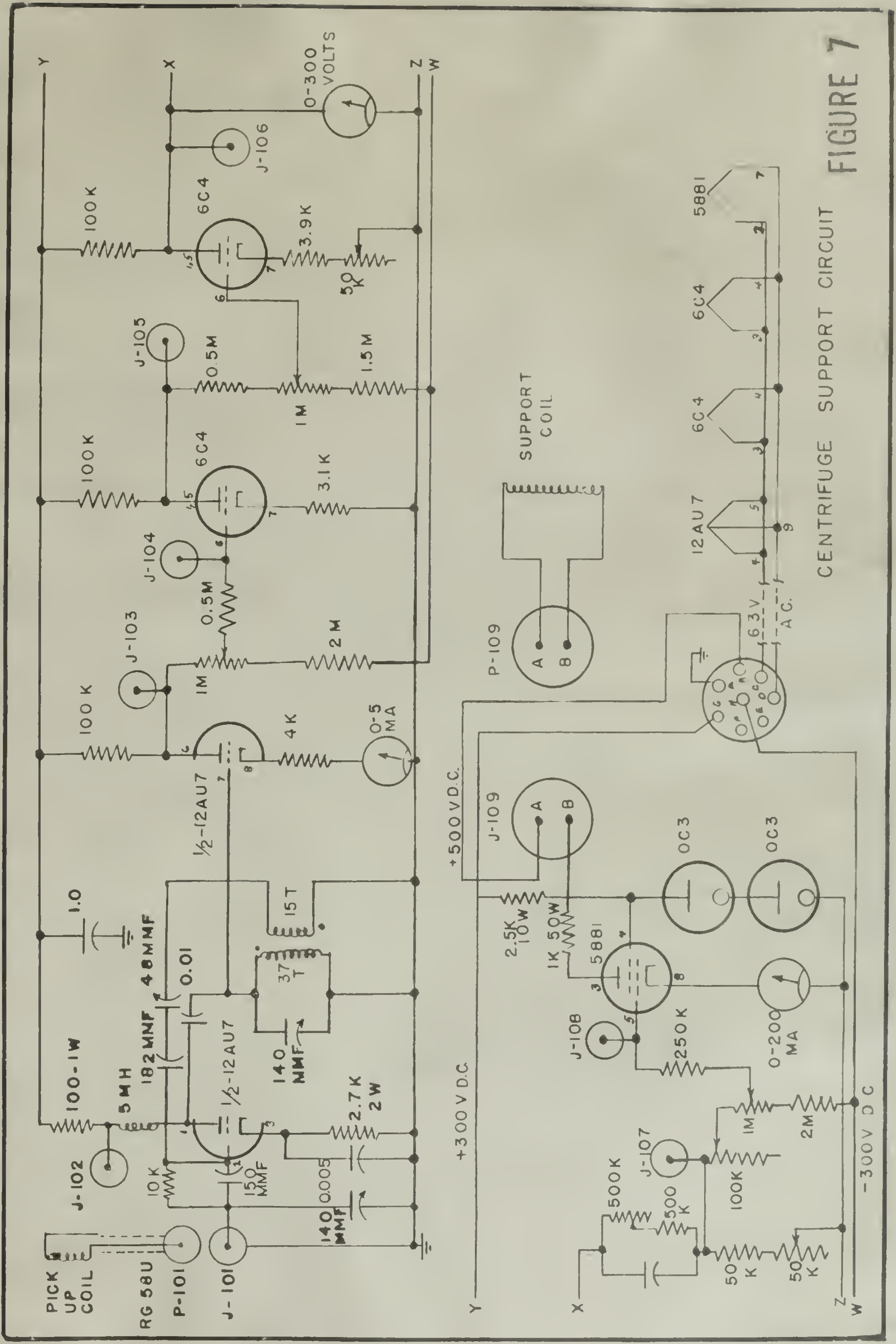
CENTRIFUGE CROSS-SECTION (VERT.)

FIGURE 5



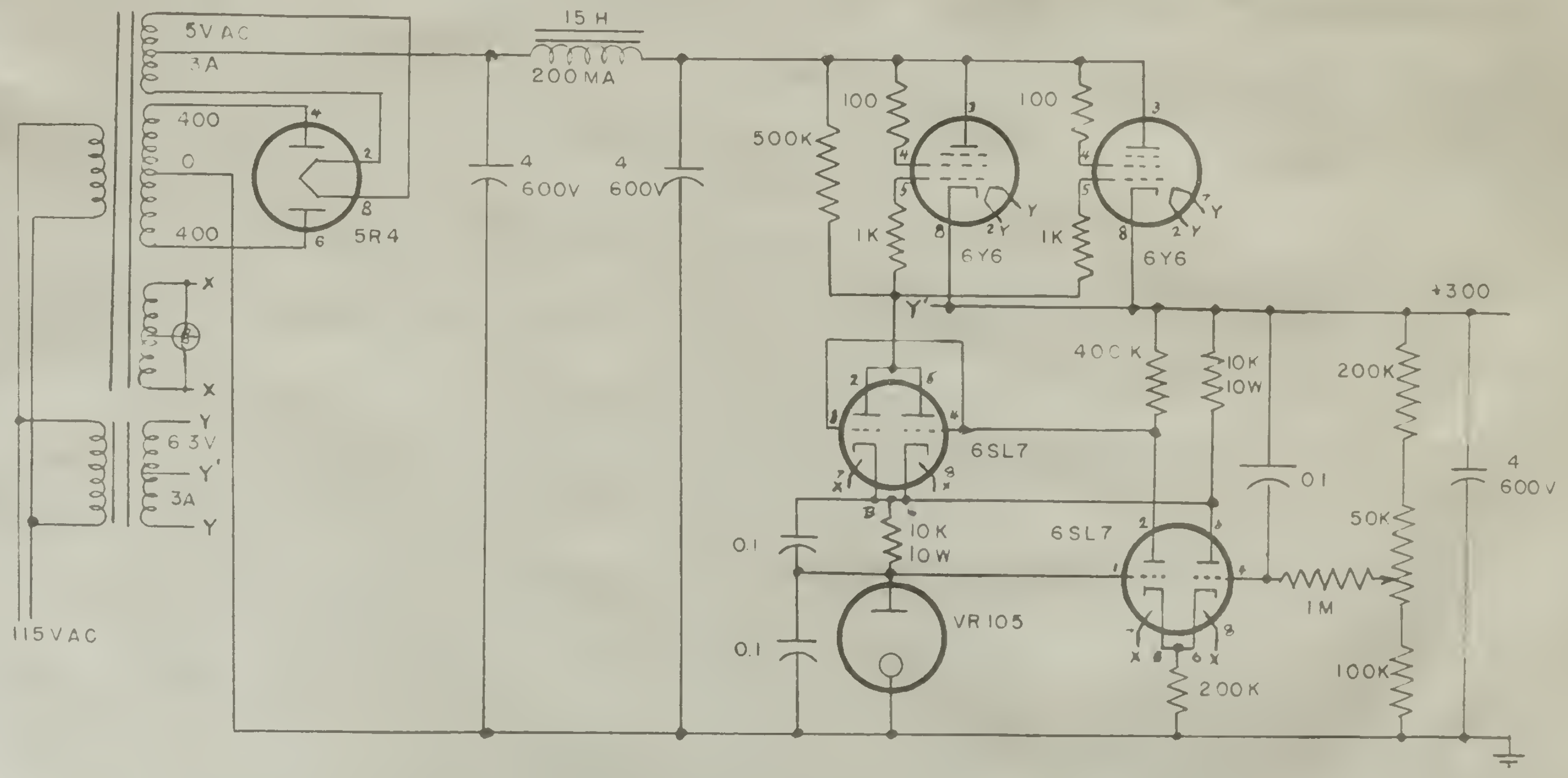
CENTRIFUGE CROSS-SECTION (HORIZ)

FIGURE 6



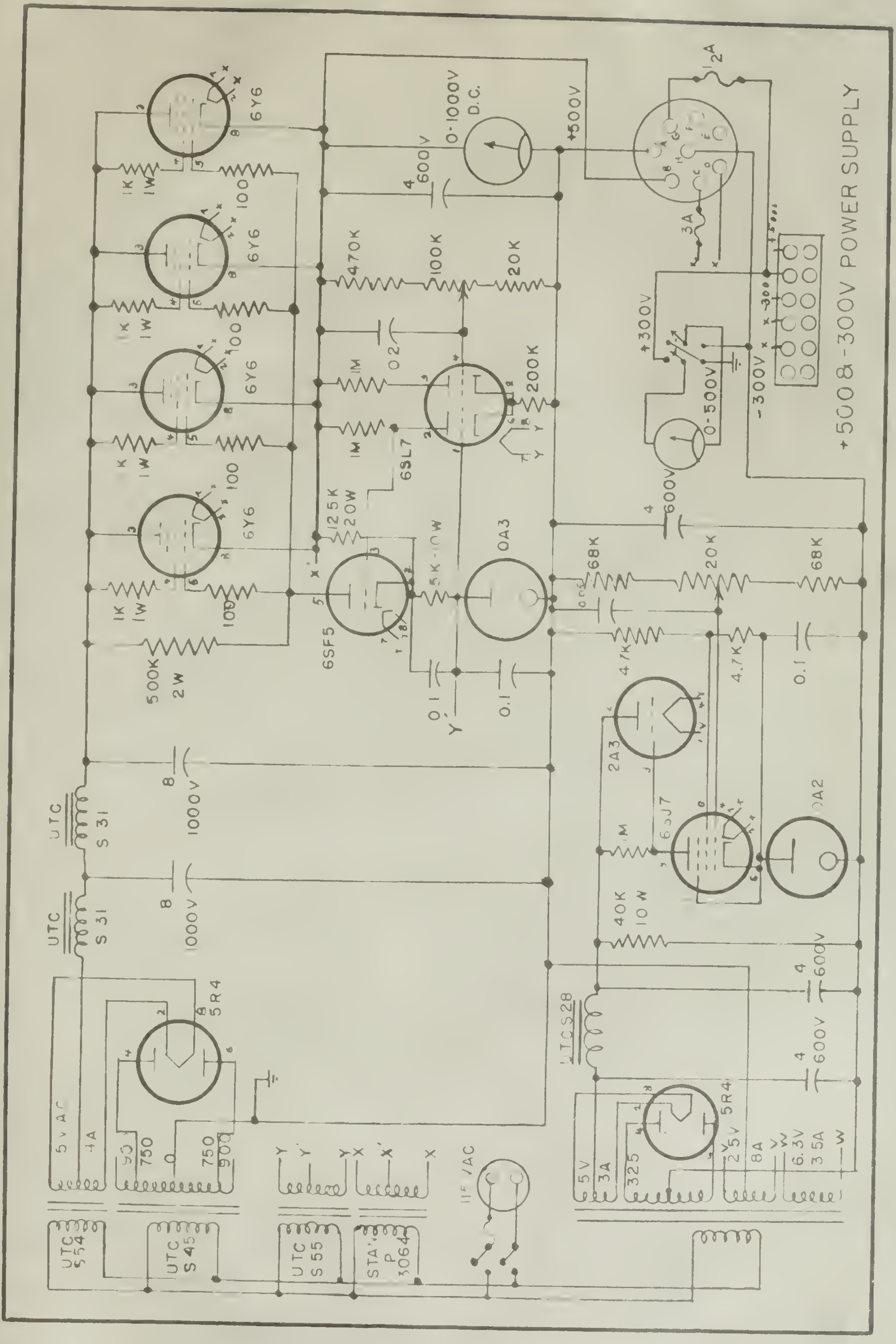
CENTRIFUGE SUPPORT CIRCUIT

FIGURE 7



+300V POWER SUPPLY

FIGURE 8



+500 & -300V POWER SUPPLY

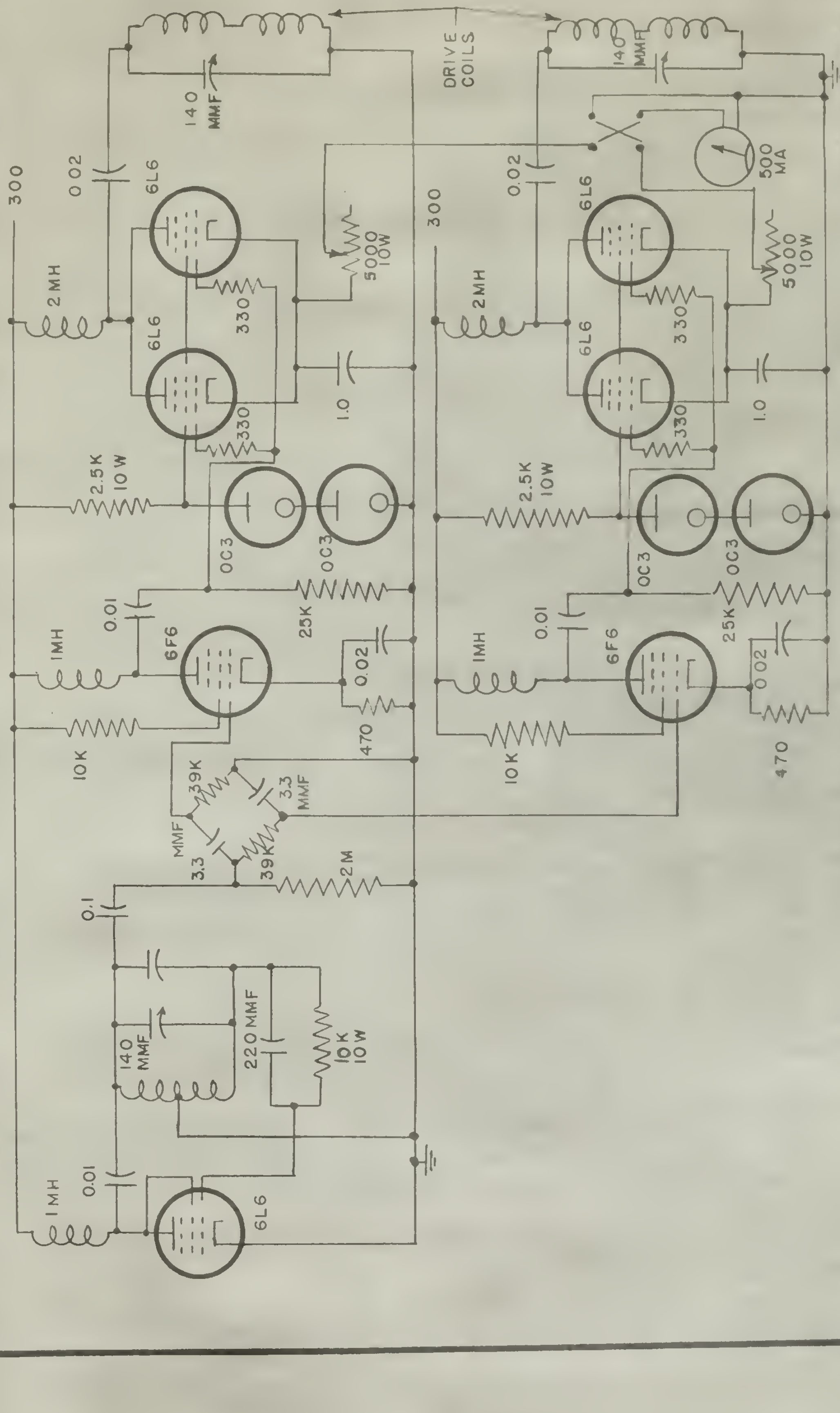


FIGURE 10

TWO PHASE DRIVE CIRCUIT

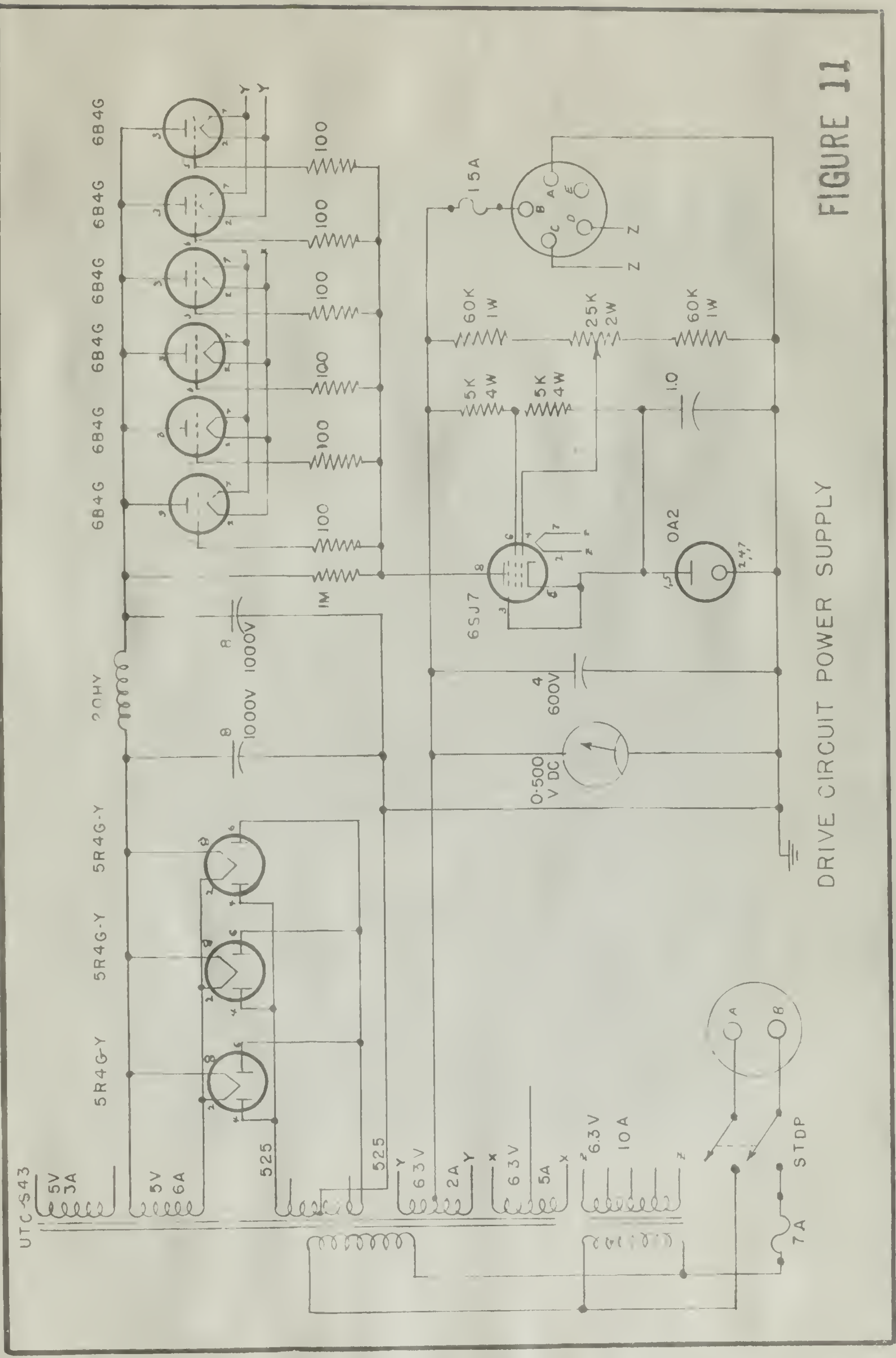
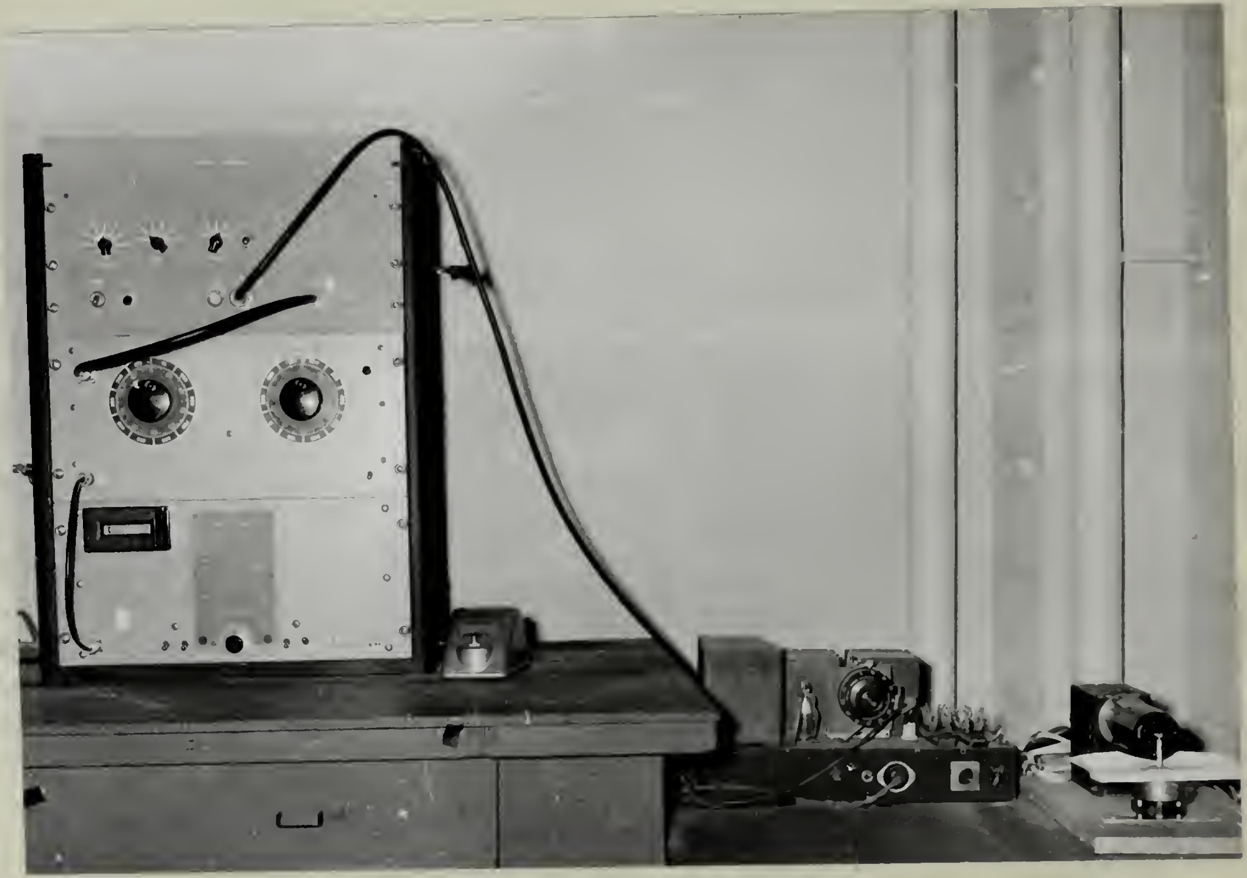


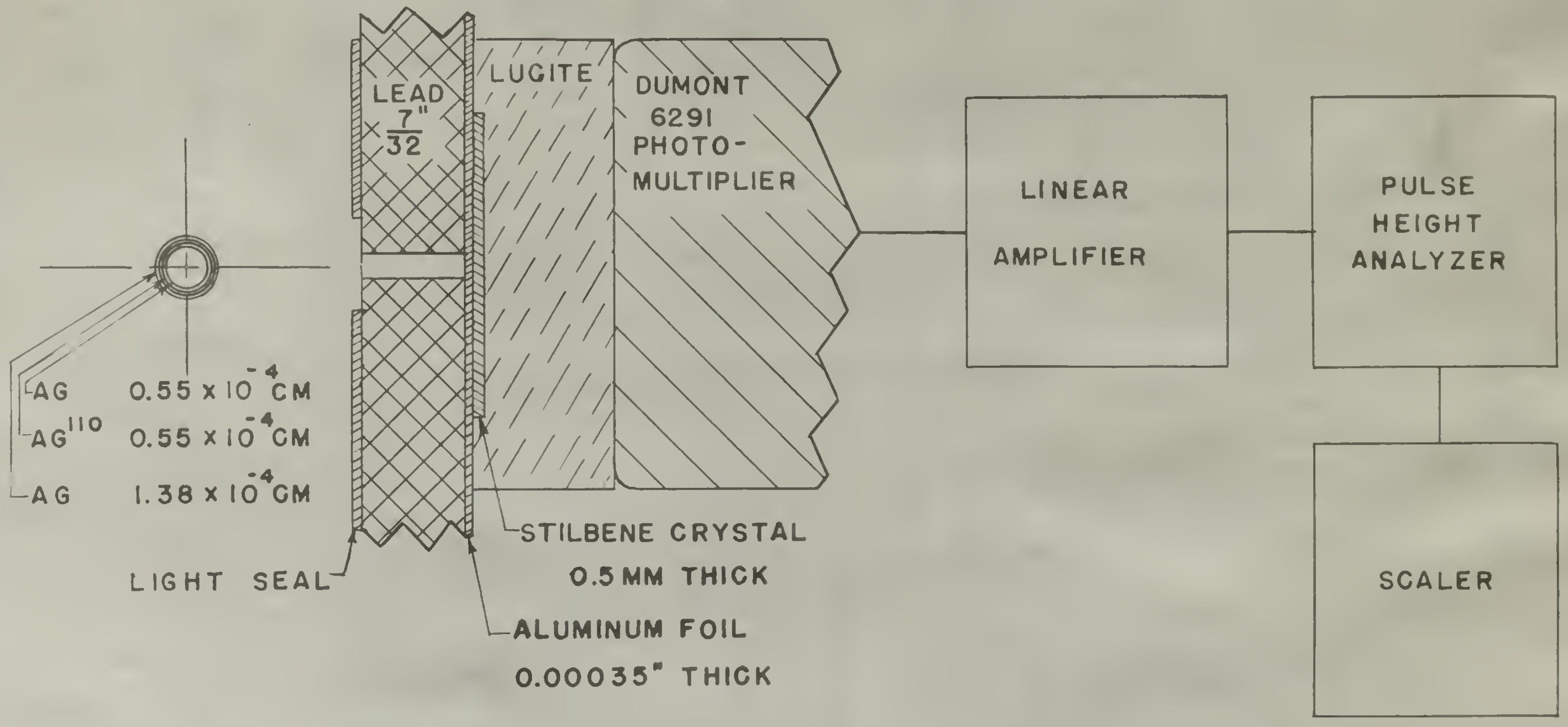
FIGURE 11

DRIVE CIRCUIT POWER SUPPLY



BETA RAY COUNTING EQUIPMENT

[illegible]


LEAD
$\frac{7''}{32}$
LUGITE
DUMONT 6291 PHOTO-MULTIPLIER
LINEAR AMPLIFIER
PULSE HEIGHT ANALYZER
SCALER
AG 0.55×10^{-4} CM
AG^{110} 0.55×10^{-4} CM
AG 1.38×10^{-4} CM
LIGHT SEAL
STILBENE CRYSTAL 0.5 MM THICK
ALUMINUM FOIL 0.00035" THICK

β RAY DETECTION EQUIPMENT AND ROTOR CONFIGURATION

FIGURE 13

APPENDIX I

TABLE I

Absorption Curve Data

Rotor No	T	N_1	S_1	N_o	S_o	N_c	N_c/N_1
I	0.46	11,896	10,280	11,460	10,201	11,550	0.970
II	0.46	9,730	10,340	9,600	10,308	9,630	0.988
III	0.92	11,023	10,211	10,563	10,189	10,580	0.961
IV	0.92	10,309	10,318	9,916	10,365	9,870	0.958
V	1.38	10,621	10,251	9,950	10,215	9,980	0.939
VI	1.38	11,223	10,103	10,524	10,162	10,430	0.931
VII	1.84	12,218	10,415	11,326	10,530	11,180	0.915
VIII	1.84	11,986	9,981	10,977	9,901	11,030	0.921

Symbols

N_1 = Number of counts per two minutes with rotor plated with 0.55×10^{-5} cm of ordinary silver and 0.55×10^{-5} cm of radioactive silver.

S_1 = Number of counts per two minutes of standard rotor as taken immediately following the counting of the test rotor with N_1 counts.

N_o = Number of counts per two minutes with rotor plated with overlay in addition to the above two layers.

S_o = Number of counts per two minutes of standard rotor as taken immediately following the counting of the test rotor with N_o counts

$N_c = N_o\ (S_1/S_o)$

T = Thickness of overlay in units of 10^{-4} centimeters.

TABLE II

Temperature Data

A. Calibration of Tempil Sticks in vacuum:

Rated Melting Temperature	Melting Temperature In Vacuum
65.6° C.	63.2 - 65.2° C.
79.4° C.	73.8 - 76.5° C.
93.3° C.	93.5 - 98.0° C.

B. Data on Rotor Temperature, when rotor was suspended on a very fine fiber in vacuum:

Rated Melting Temperature of Tempil Stick	Sustaining Drive	Sustaining Drive and Light	Full Drive and Light
51.7° C.	melted	did not melt	did not melt
65.6° C.	did not melt	melted	melted
79.4° C.	did not melt	did not melt	did not melt
93.3° C.	did not melt	did not melt	did not melt

TABLE III

Diffusion Data at 200,000 revolutions per second and 72° C.

Elapsed Time (Hours)	N_r	N_s	N_{rc}	N_{rc}/N_{ri}	Percent Change
0.0	5061	5486	----	--------	-----
1.4	5194	5440	5230	1.032	3.2
6.4	4595	4806	5240	1.035	3.5
0.0	4537	4991	-----	-----	-----
3.0	4514	4792	4695	1.034	3.4
5.8	4565	4820	4730	1.042	4.2
10.3	4953	5332	4648	1.027	2.7
14.8	4948	5156	4780	1.052	5.2
0.0	10966	4551	----	----	----
0.9	12195	4934	11260	1.024	2.4

N_r = Counts of test rotor per minimum two minutes

N_s = Counts of standard rotor per two minutes

N_{rc} = Adjusted counts of rotor per two minutes; equals

$$\frac{N_r\ (N_s \text{ at time } 0.0 \text{ hours})}{(N_s \text{ at the elapsed time of } N_r)}$$

N_{ri} = N_r at time 0.0 hours.

TABLE IV

Diffusion Data at 400,000 revolutions per second and 72° C.

Elapsed Time (Hours)	N_r	N_s	N_{rc}	N_{rc}/N_{ri}	Percent Change
0.0	12,314	5032	-----	--------	------
1.2	12,613	5048	12,600	1.022	2.2
0.0	11,723	5380	-----	-----	-----
1.7	11,614	5185	12,070	1.029	2.9
0.0	10,063	5319	-----	----	-----
2.6	10,289	5263	10,410	1.033	3.3
0.0	9,080	5133	------	-----	-----
3.7	9,327	5112	9,360	1.030	3.0
0.0	10,299	5052	-----	-----	------
5.7	10,560	5034	10,580	1.025	2.5
9.3	10,612	5069	10,590	1.029	2.9

Symbols:

N_r = Counts of test rotor per two minutes

N_s = Counts of standard rotor per two minutes

N_{rc} = Adjusted counts of test rotor per two minutes

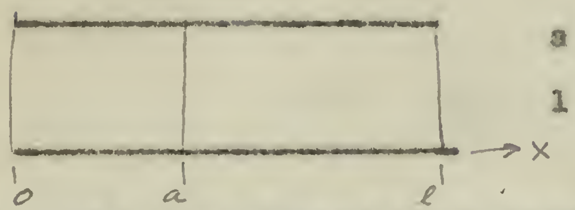
equals $$N_r \frac{(N_s \text{ at time } 0.0 \text{ hrs})}{(N_s \text{ at the elapsed time of } N_r)}$$

N_{ri} = N_r at time 0.0 hours

APPENDIX II

CALCULATIONS

A. Absorption Coefficient



$a \cong 0.55 \times 10^{-4}$ cm.

$1 \cong$ thickness of overlay

All counts are measured by a crystal located at some point $x > a \neq 1$.

N_f(No. of counts with an overlay of thickness, 1)

$$N_f = \frac{1}{a}\int_0^a e^{-\lambda(\ell+a-x)}dx = \frac{e^{-\lambda\ell} - e^{-\lambda(a+\ell)}}{a\lambda}$$

N_i (No. of counts without an overlay, $1 \cong 0$).

$$N_i = \frac{1-e^{-a\lambda}}{a\lambda}$$

$$\frac{N_f}{N_i} = \frac{e^{-\lambda\ell} - e^{-\lambda(\ell+a)}}{1-e^{-a\lambda}}$$

Expanding the powers of e in series,

$$\frac{N_f}{N_i} = \left[1-\left(1-a\lambda+\frac{a^2\lambda^2}{2}\right)\right]^{-1}\cdot\left[1-\lambda\ell+\frac{\lambda^2\ell^2}{2}-\left(1-\lambda\ell-\lambda a+\frac{\lambda^2\ell^2}{2}+\frac{\lambda^2a^2}{2}+\lambda\ell a\right)\right]$$

Solving for λ,

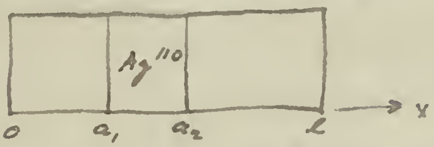
$$\lambda = \frac{1}{\frac{a}{2}+\frac{\ell}{\left(1-\frac{N_f}{N_i}\right)}}$$

ℓ	$\frac{N_f}{N_i}$	λ
0.46×10^{-4} cm.	0.979	4.57×10^{2} cm^{-1}
0.92×10^{-4} cm.	0.959	4.46×10^{2} cm^{-1}
1.38×10^{-4} cm.	0.935	4.72×10^{2} cm^{-1}
1.84×10^{-4} cm.	0.918	4.52×10^{2} cm^{-1}

4.57×10^{2} cm^{-1} Ave.

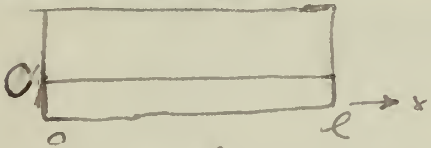
B. Calculation of the maximum observable change in the counting rate after equilibrium has been reached by thermal diffusion.

The number of counts per unit time before diffusion starts is:



$$N_i = \frac{1}{a_2-a_1}\int_{a_1}^{a_2} e^{-\lambda(l-x)}\,dx = \frac{e^{-\lambda(l-a_2)} - e^{-\lambda(l-a_1)}}{a_2-a_1}$$

The number of counts per unit time after equilibrium has been reached, is:



$$N_f = \frac{1}{l}\int_0^l e^{-\lambda(l-x)}\,dx = \frac{1-e^{-\lambda l}}{\lambda l}$$

The ratio, N_f/N_i which is the maximum observable change after a very long period of time is:

$$\frac{N_f}{N_i} = \frac{1-e^{-\lambda l}}{e^{-\lambda(l-a_2)} - e^{-\lambda(l-a_1)}} \cdot \frac{a_2-a_1}{l}$$

$a_1 = 0.55 \times 10^{-4}$ cm

$a_2 = 1.10 \times 10^{-4}$ cm

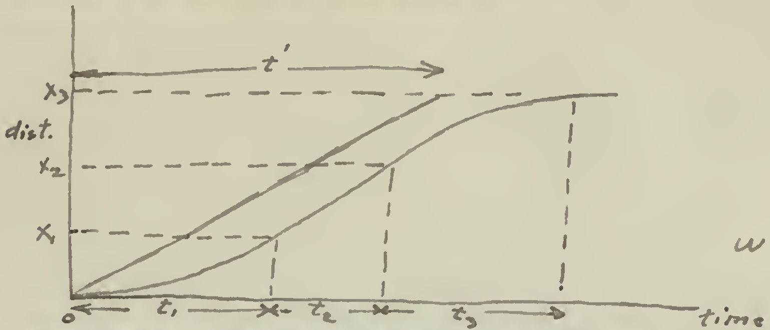
$l = 2.38 \times 10^{-4}$ cm

$\lambda = 4.57 \times 10^{2}$ cm^{-1}

$$\frac{N_f}{N_i} = \frac{1-0.8932}{0.9393-0.9158} \cdot \frac{0.55}{2.48} = 1.005$$

C. Determination of an effective time to compensate for the affect of variable fields on diffusion during the acceleration and deceleration periods.

The acceleration and deceleration remained constant during their respective periods.



ω = constant speed of test

Distance diffused during time, t; $x = C\omega^2 t$ where $C = \frac{M\Delta D}{RT}$

Acceleration: $\omega' = \omega \frac{t}{t_1}$

$$X_1 = \int_0^{t_1} C\omega^2 \left(\frac{t}{t_1}\right)^2 dt = C\omega^2 \frac{t_1}{3}$$

Constant Speed: $\omega' = \omega$

$$X_2 - X_1 = \int_{t_1}^{t_1+t_2} C\omega^2 dt = C\omega^2 t_2$$

Deceleration: $\omega' = \omega\left[1 - \frac{t-(t_1+t_2)}{t_3}\right]$

$$X_3 - X_2 = \int_{t_1+t_2}^{t_1+t_2+t_3} C\omega^2\left[1 - \frac{t-(t_1+t_2)}{t_3}\right]^2 dt = C\omega^2 \frac{t_3}{3}$$

Total distance moved during the entire time is:

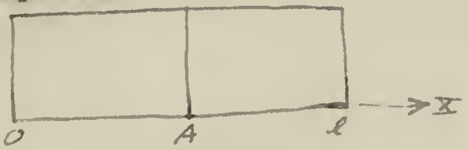
$$\overline{X} = C\omega^2\left[\frac{t_1}{3} + t_2 + \frac{t_3}{3}\right]$$

This same distance moved would have been obtained by operating at a constant speed for an effective time,

$$t' = \frac{\overline{X}}{C\omega^2}$$

$$t' = \frac{t_1}{3} + t_2 + \frac{t_3}{3}$$

D. Solution of Fick's one dimensional equations for the concentration of the radioisotope as a function of time and space.



$$x = \frac{X}{\ell}$$
$$t = \frac{TF}{\ell}$$
$$\alpha = \frac{D}{F\ell}$$

$$\frac{\partial C(X,T)}{\partial T} = D\,\frac{\partial^2 C(X,T)}{\partial X^2} - F\,\frac{\partial C(X,T)}{\partial X}$$

$$\frac{\partial C(x,t)}{\partial t} = \alpha\,\frac{\partial^2 C(x,t)}{\partial x^2} - \frac{\partial C(x,t)}{\partial x}$$

To separate the variables, let $C(x,t) = T(t)\cdot\mathcal{X}(x)$ (1)

Setting both sides equal to a constant, $-q$;

$\frac{1}{T}\frac{\partial T}{\partial t} = -q = \frac{\alpha}{\mathcal{X}}\frac{\partial^2\mathcal{X}}{\partial x^2} - \frac{1}{\mathcal{X}}\frac{\partial\mathcal{X}}{\partial x}$ is obtained.

The solution of the left hand side is: $T = C_1 e^{-qt}$ (2)

The solution of the right hand side is obtained as follows:

$$\frac{\partial^2\mathcal{X}}{\partial x^2} - \frac{1}{\alpha}\frac{\partial\mathcal{X}}{\partial x} + \frac{q}{\alpha}\mathcal{X} = 0$$

$$\left(r^2 - \frac{1}{\alpha}r + \frac{q}{\alpha}\right)\mathcal{X} = 0$$

$$r = \frac{1}{2\alpha}\left(1 \pm \sqrt{1-4q\alpha}\right) = \frac{1}{2\alpha}\left(1 \pm i\sqrt{4q\alpha-1}\right)$$

then $\mathcal{X} = C_2 e^{\frac{1}{2\alpha}(1+i\sqrt{4q\alpha-1})x} + C_3 e^{\frac{1}{2\alpha}(1-i\sqrt{4q\alpha-1})x}$

By letting $p = \frac{\sqrt{4q\alpha-1}}{2\alpha}$ (3)

$$\mathcal{X} = e^{\frac{x}{2\alpha}}\left[C_2'\cos px + C_3'\sin px\right]$$

Using the condition that $C(x,t) = 0$ at $X = \ell$ or $x = 1$ for all times, t; $\mathcal{X}$ must $= 0$ thereby determining C_3'.

$$C_3' = -C_2'\cot p$$

q is found by solving (3)

$$q = \frac{1+4\alpha^2 p^2}{4\alpha}$$

Fick's equation for the diffusion current is:

$$J = -\alpha \frac{dC(x,t)}{dx} + C(x,t) \tag{4}$$

By using the condition that $J = 0$ at $X = x = 0$ for all time, and substituting the product of (2) and (3) for (1) in (4);

$$0 = -\alpha\left(\frac{1}{2\alpha}\right)(C_2')(1+0) - (\alpha)(1)(C_2')(0 - p\cot p) + C_2'$$

$\frac{\tan p}{p} = -2\alpha$ is obtained which results in an infinite number of p's with a corresponding infinite number of q's .

Thus $X_0 = e^{\frac{x}{2\alpha}} \sum_{i=1}^{\infty} C_{pi} (\cos p_i x - \cot p_i \sin p_i x)$ (5)

and the concentration becomes:

$$C(x,t) = e^{\frac{x}{2\alpha}} \sum_{i=1}^{\infty} C_i e^{-q_i t} (\cos p_i x - \cot p_i \sin p_i x) \tag{6}$$

Evaluation of the constant, C_i;

Let $u_i(x) = \cos p_i x - \cot p_i \sin p_i x$

Then at $t = 0$

$$C(x,0)\, e^{-\frac{x}{2\alpha}} = \sum_{i=1}^{\infty} C_i\, u_i(x) \tag{7}$$

Multiplying both sides of (7) by $u_j(x)$ and integrating over dx yields:

$$\int_0^1 C(x,0) e^{-\frac{x}{2\alpha}} u_j \, dx = \int_0^1 \sum_{i=1}^{\infty} C_i\, u_i(x)\, u_j(x)\, dx \tag{8}$$

The right hand side of (8) reduces to:

$$C_i\, \delta_{ij} \frac{1 + 2\alpha + \tan^2 p_i}{2\tan^2 p_i} = \delta_{ij} \frac{1 + 2\alpha + 4\alpha^2 p_i^2}{8\alpha^2 p_i^2} C_i$$

If all of the radioactive atoms are located at the distance, a, $C(x,0) = \frac{1}{l}\,\delta(x-a)$

to satisfy the condition

$$\int_0^1 \frac{1}{1}\, \delta(x-a)\, d(x) = 1$$

Upon substitution, the left hand side of (8) becomes:

$$\int_0^1 e^{-\frac{x}{2\alpha}} u_j(x) \frac{1}{\ell} \delta(x-a)\, dx$$

Since values can be obtained only when $x = 0$, the expression reduces to: $e^{-\frac{a}{2\alpha}} u_j(a) \frac{1}{\ell} \int_0^1 dx$

which upon integration becomes:

$$\frac{1}{\ell} e^{-\frac{a}{2\alpha}} (\cos p_j a - \cot p_j \sin p_j a)$$

Recombining both parts of the equation (8), we obtain:

$$\frac{1}{\ell} e^{-\frac{a}{2\alpha}} (\cos p_j a - \cot p_j \sin p_j a) = C_i \delta_{ij} \frac{1+2\alpha+4\alpha^2 p_i^2}{8\alpha^2 p_i^2}$$

which, since j must equal i to obtain a value for the right hand side, yields the values for C_i

$$C_i = \frac{1}{\ell} e^{\frac{a}{2\alpha}} (\cos p_i a - \cot p_i \sin p_i a) \frac{8\alpha^2 p_i^2}{1+2\alpha+4\alpha^2 p_i^2} \qquad (9)$$

Substituting (9) into (6), the equation for the concentration becomes:

$$C(x,t) = \frac{1}{\ell} e^{\frac{x-a}{2\alpha}} \sum_{i=1}^{\infty} e^{-q_i t} \frac{8\alpha^2 p_i^2}{1+2\alpha+4\alpha^2 p_i^2} (\cos p_i a - \cot p_i \sin p_i a)(\cos p_i x - \cot p_i \sin p_i x) \qquad (10)$$

and (4) for $J(1,t$ becomes:

$$\frac{1}{F} J(1,t) = -\frac{\alpha}{\ell} e^{-\frac{x-a}{2\alpha}} \sum_{i=1}^{\infty} e^{-q_i t} \frac{8\alpha^2 p_i^2}{1+2\alpha+4\alpha^2 p_i^2} (\cos p_i a - \cot p_i \sin p_i a)(-\sin p_i x - \cot p_i \cos p_i x)\, p_i \qquad (11)$$

E. Transportation of the solutions to the Fick one dimensional equations from concentration to counting rates.

At any time, t, the amount of radioactive silver diffused to the outer surface, $x = 1$ is:

$$\frac{\ell}{F} \int_0^t J(1,t')\,dt' = \frac{\ell}{F} \int_0^{\infty} J(1,t')\,dt' - \frac{\ell}{F} \int_t^{\infty} J(1,t')\,dt' \qquad (12)$$

Substitution of (11) for $\frac{1}{F}\ J(1,t')$ results in:

$$= 1-\alpha e^{\frac{1-a}{2\alpha}} \sum_{i=1}^{\infty} e^{-q_i t}\frac{1}{q_i}\,\frac{8\alpha^2 p_i^2}{1+2\alpha+4\alpha^2 p_i^2}\left(\cos p_i a - \cot p_i \sin p_i a\right)$$

$$p_i \sin p_i \left(1+\frac{1}{4\alpha^2 p_i}\right);$$

which reduces to:

$$= 1-\alpha e^{\frac{1-a}{2\alpha}} \sum_{i=1}^{\infty} e^{-q_i t}\frac{8\alpha^2 p_i^2}{1+2\alpha+4\alpha^2 p_i^2}\sin p_i (1-a) \qquad (13)$$

If we consider the counting rate for the particles at the inner face, $x = 0$ to be one, then any movement towards the outer face would result in an increase by $e^{\lambda \bar{X}}$ or $e^{\mu x}$ where $\mu = \lambda \ell$ and λ is the absorption coefficient calculated in part A of this appendix. Therefore the counting rate observed at a time, t, as the result of the atoms diffusing to the free surface, $x = 1$ is:

$$e^{-\mu}\left[1-\alpha e^{\frac{1-a}{2\alpha}} \sum_{i=1}^{\infty} e^{-q_i t}\frac{8\alpha^2 p_i^2}{1+2\alpha+4\alpha^2 p_i^2}\sin p_i(1-a)\right] \qquad (14)$$

Let us now consider the change in the counting rate resulting from the atoms distributed within the films.

$$C(x,t) = \frac{1}{\ell}\, e^{\frac{x-a}{2\alpha}} \sum_{i=1}^{\infty} e^{-q_i t}\frac{8\alpha^2 p_i^2}{1+2\alpha+4\alpha^2 p_i^2}\,\frac{1}{\sin^2 p_i}\,\sin p_i(1-a)\sin p_i(1-x)$$

$$= \frac{1}{\ell}\, e^{\frac{x-a}{2\alpha}} \sum_{i=1}^{\infty} e^{-q_i t}\frac{8\alpha^2 p_i^2}{1+2\alpha+4\alpha^2 p_i^2}\left(1+\frac{1}{4\alpha^2 p_i^2}\right)\sin p_i(1-a)\sin p_i(1-x) \qquad (15)$$

Multiplying (15) by $e^{-\mu x}$ and integrating over x from 0 to 1, we obtain:

$$e^{-\frac{a}{2\alpha}}\int_0^1 e^{-q_i t}\, e^{\left(\frac{1}{2\alpha}+\mu\right)x}\left(1+\frac{1}{4\alpha^2 p_i^2}\right)\frac{8\alpha^2 p_i^2}{1+2\alpha+4\alpha^2 p_i^2}\sin p_i(1-a)\sin p_i(1-x)\,dx$$

which is of the form:

$$\int_0^1 e^{\gamma x}\sin p_i(1-x)\,dx = \frac{1}{\gamma^2+p_i^2}\left[p_i e^{\gamma} - \gamma \sin p_i - p_i \cos p_i\right]$$

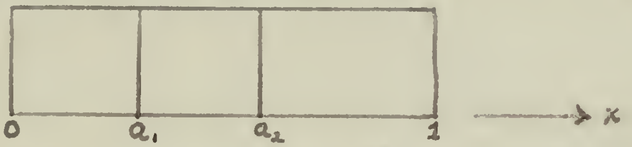
Substituting $\left(\frac{1}{2\alpha}+\mu\right)$ for γ the counting rate at time, t, resulting from the atoms distributed in the films, is:

$$e^{-\frac{a}{2\alpha}}\sum_{i=1}^{\infty} e^{-q_i t}\left(1+\frac{1}{4\alpha^2 p_i^2}\right)\frac{8\alpha^2 p_i^2}{1+2\alpha+4\alpha^2 p_i^2}\sin p_i(1-a)\frac{1}{\left(\frac{1}{2\alpha}+\mu\right)^2+p_i^2}\cdot$$

$$\left[p_i e^{\left(\frac{1}{2\alpha}+\mu\right)}-\left(\frac{1}{2\alpha}+\mu\right)\sin p_i - p_i \cos p_i\right] \qquad (16)$$

The total counting rate at time, t, is the sum of (14) and (16). This is the counting rate when starting with an initial delta function distribution.

Since the problem concerned with this experiment starts with a relatively thick film, $a_1 < x < a_2$ containing the radioisotope, it is necessary to develop a correction to compensate for this initial distribution.



$$\int_{a_1}^{a_2} e^{-\frac{a}{2\alpha}}\sin p_i(1-a)\,da = \frac{e^{-\frac{a_1}{2\alpha}}}{\left(\frac{1}{2\alpha}\right)^2+p_i^2}\left[\frac{1}{2\alpha}\sin p_i(1-a_1) - p_i\cos p_i(1-a_1)\right]$$

$$-\frac{e^{-\frac{a_2}{2\alpha}}}{\left(\frac{1}{2\alpha^2}\right)^2+p_i^2}\left[\frac{1}{2\alpha}\sin p_i(1-a_2)-p_i\cos p_i(1-a_2)\right] \qquad (17)$$

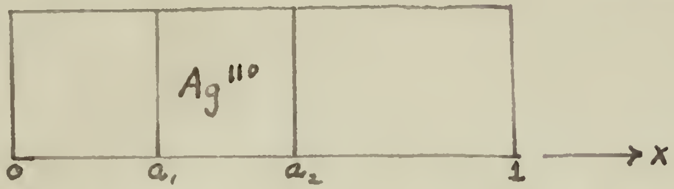
Letting this expression be designated by $G\left(\frac{1}{2\alpha}, p_i, a_1, a_2\right)$ and intro- using this into equations (14) and (15) for the correction from the delta function distribution we obtain for the counting rate a time, t :

$$N_t = e^{\mu}\left[1-\alpha\frac{e^{\frac{1}{2\alpha}}}{(a_2-a_1)}\sum_{i=1}^{\infty} e^{-q_i t}\frac{8\alpha p_i}{1+2\alpha+4\alpha^2 p_i^2}\, G\left(\frac{1}{2\alpha}, p_i, a_1, a_2\right)\right]$$

$$+\frac{1}{(a_2-a_1)}\sum_{i=1}^{\infty} e^{-q_i t}\left(1+\frac{1}{4\alpha^2 p_i^2}\right)\frac{8\alpha^2 p_i^2}{1+2\alpha+4\alpha^2 p_i^2}\cdot\frac{1}{\left(\frac{1}{2\alpha}+\mu\right)^2+p_i^2}\cdot$$

$$\left[p_i e^{\frac{1}{2\alpha}+\mu}-\left(\frac{1}{2\alpha}+\mu\right)\sin p_i - p_i\cos p_i\right] G\left(\frac{1}{2\alpha}, p_i, a_1, a_2\right).$$

F. Derivation for the expression of the counting rate at time, $t=0$, for the geometry of the films, and assuming that the counting rate for the radioisotope at $t=0$ is one.



The number of counts before diffusion starts is:

$$N_i = \frac{1}{a_2-a_1}\int_{a_1}^{a_2} e^{\mu x}\,dx = \frac{e^{\mu a_2}-e^{\mu a_1}}{\mu(a_2-a_1)}$$

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